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Disentangling the Coupled Origins of Li^+ Ion Transport in LATP through Hierarchical Modeling

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Abstract

Aliovalent substitution in solid electrolytes simultaneously modifies carrier concentration, framework chemistry, structure, and disorder, hindering mechanistic understanding of ion transport. Here, we combine a fine-tuned machine-learning foundation potential, energy-landscape analysis, and molecular dynamics simulations to investigate Li^+ ion diffusion across the full compositional range of the NASICON electrolyte $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ ($0 \leq x \leq 2$). A MACE foundation model trained on a single composition transfers across the substitution range, enabling efficient simulations of large disordered systems.

By systematically separating carrier-concentration, framework, and structural contributions, we identify the mechanisms governing transport across the LATP composition range. Al substitution reshapes the framework potential, producing trapping at low Al content and connected low-energy pathways at high Al content, but does not itself explain the transport trend. Instead, additional Li lowers effective barriers through ion-ion interactions and drives the initial increase in diffusivity. The decline at high substitution emerges only when composition-dependent cell relaxation is considered together with framework dynamics and is associated with reduced cell volume and stronger Li-O interactions.

Beyond explaining the non-monotonic transport behavior of LATP, this work shows how computational models of increasing physical complexity can isolate mechanisms that are difficult to disentangle experimentally or in fully coupled simulations. This hierarchical strategy offers a broadly applicable approach to composition-structure-transport relationships in configurationally complex materials.

1 Introduction

Solid ceramic electrolytes are of considerable interest for all-solid-state batteries due to their thermal stability, non-flammability, and electrochemical robustness.[1, 2] Among the diverse families of solid electrolytes, NASICON-type materials have attracted particular attention owing to their three-dimensional diffusion networks, structural stability, and compositional flexibility.[3, 4] These characteristics make NASICON compounds an attractive platform for studying how chemical substitution influences ionic transport in crystalline solids.

A prominent example is lithium titanium phosphate, $\text{LiTi}_2(\text{PO}_4)_3$ (LTP), and its aliovalently substituted derivative $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ (LATP). Substitution of Ti^{4+} by Al^{3+} introduces additional Li^+ ions to maintain charge neutrality and results in a characteristic non-monotonic dependence of ionic conductivity on composition.[3, 5] Experimentally, the conductivity increases with increasing x up to approximately $x \approx 0.3$, before decreasing at higher substitution levels.[3] Although this behavior has been observed for several decades, its microscopic origin remains incompletely understood.

Several mechanisms have been proposed to explain how Al substitution influences Li^+ transport in LATP.[6] Changes in framework chemistry modify local Li^+ -framework interactions and alter the potential energy landscape for diffusion. Simultaneously, the increase in Li^+ concentration affects site occupancies, ion-ion correlations, and migration mechanisms. Structural changes, including variations in cell volume, local distortions, and bottleneck geometries, further influence diffusion pathways by modifying the accessible free volume. Because these effects are strongly coupled, determining their relative contributions to ionic transport remains a challenge.

In LATP, Li^+ transport is commonly described in terms of hopping between M1 sites through interstitial M2 configurations within the NASICON framework shown in Fig. 1, with additional M1/2 split sites emerging as the Li^+ concentration increases.[3, 7] These additional sites contribute to the connectivity of the diffusion network and have been associated with interstitial migration mechanisms.[7, 8] Al substitution has also been shown to locally stabilize Li^+ ions, creating heterogeneous energy landscapes and preferential site occupations.[7] At higher substitution levels, reductions in conductivity have been attributed to both intrinsic effects, including structural distortions and modified local interactions, and extrinsic effects such as grain boundaries and secondary-phase formation.[9–11]

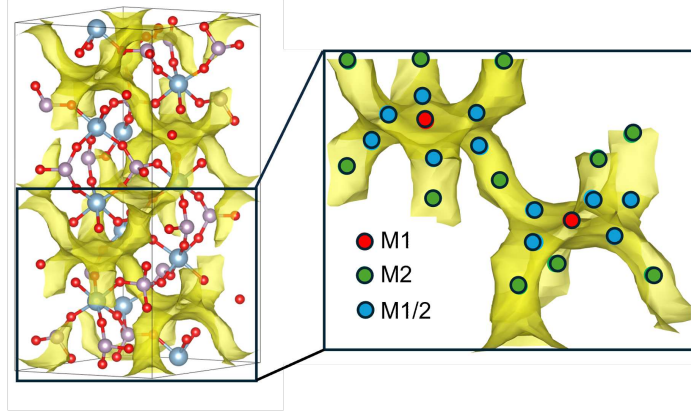


Fig. 1 Diffusion network in LATP unit cell with framework atoms (red = O, blue = Ti, purple = Al) and the potential energy iso-surface of diffusing Li^+ ions. Inset zooms in on the potential energy surface illustrating the location of energy minima sites: M1 global energy minima (red), M2 local interstitial sites (green), as well as M1/2 split sites, which emerge through the addition of Li^+ ions.

Atomistic simulations offer a powerful route to disentangle the competing effects of carrier concentration, framework chemistry, structure, and disorder. However, significant computational challenges remain. Previous studies have often been limited to small periodic cells, short simulation times, or restricted compositional ranges, thereby underrepresenting substitutional disorder and limiting access to the full configurational space.[12, 13] Furthermore, approaches based on minimum-energy pathways or static structures do not fully capture collective ion-ion interactions or the influence of framework dynamics, both of which play an important role in ionic transport.[14] Consequently, obtaining a unified picture of how carrier concentration, framework chemistry, structural relaxation, and disorder collectively govern transport across composition space remains difficult.

Simulating larger and more compositionally diverse systems over timescales sufficient to observe diffusion requires atomistic models that are considerably more efficient than direct DFT calculations. Machine-learning interatomic potentials provide this efficiency while retaining close agreement with first-principles reference data.[13] In particular, foundation models trained on chemically and structurally diverse datasets provide transferable starting points across a broad range of material classes.[15] However, they generally require fine-tuning to achieve sufficient accuracy for a specific material system. The challenge is therefore to obtain this accuracy without generating reference data across the entire compositional and configurational space. Fine-tuning using limited but chemically representative data may provide an efficient route to combining first-principles accuracy with the extensive configurational exploration required for compositionally disordered materials.

In this study, we combine energy-landscape analysis and molecular dynamics simulations to determine how carrier concentration, framework chemistry, and structural response govern Li^+ transport across the complete compositional range of

$\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ ($0 \leq x \leq 2$). Single-particle energy landscapes isolate interactions between Li^+ ions and the substituted framework, while multi-particle calculations introduce ion-ion interactions and allow the Li and Al concentrations to be varied independently. Molecular dynamics simulations then incorporate framework flexibility, composition-dependent structural relaxation, and configurational disorder. Applying this hierarchy to large disordered systems across the full substitution range is made computationally feasible by a fine-tuned MACE foundation potential. By comparing these complementary descriptions, we identify the contributions responsible for both the initial enhancement of diffusion and its decrease at high Al content. More generally, the study provides a systematic computational strategy for disentangling coupled transport mechanisms in aliovalently substituted ionic conductors.

2 Computational Details

To disentangle the coupled effects of carrier concentration, framework chemistry, structural relaxation, and configurational disorder on Li^+ ion transport, we employ a hierarchy of computational descriptions with progressively increasing physical complexity. The workflow is designed to separately quantify the contributions of Li^+ -framework interactions, Li^+ - Li^+ interactions, Li^+ concentration, framework flexibility, and substitution-induced structural changes across the full LATP composition space.

Within this framework, the Ionic TuTraSt method[16, 17] is used to decompose the free-energy landscape into distinct Li^+ -framework and Li^+ - Li^+ contributions. This decomposition enables a direct assessment of how Al substitution modifies the host-framework potential experienced by mobile ions. Furthermore, the effect of carrier concentration can be isolated by independently varying the number of Li^+ ions while maintaining a fixed framework potential. Structural and dynamical effects that are inaccessible within the fixed-framework approximation of Ionic TuTraSt are subsequently captured using MD simulations, allowing the influence of framework flexibility, cell relaxation, and local structural rearrangements on diffusion to be evaluated.

A central challenge in aliovalently substituted materials is the large configurational space arising from substitutional disorder. In LATP, the number of possible Al/Ti arrangements grows rapidly with substitution level and simulation-cell size. To sample this configurational variability while reducing artificial periodicity effects, we employ enlarged supercells and multiple independent substitutional configurations at each composition.

To efficiently explore this compositionally and configurationally complex materials space, we employ the MACE-MPA0 foundation model.[18] Foundation models are designed to provide transferable interatomic representations across diverse chemical and structural environments and can be adapted to specific materials systems through limited fine-tuning. Here, we fine-tune the model using training data from a single LATP composition and assess its transferability across the entire substitution range. The resulting potential reproduces near first-principles accuracy for structures, energetics, migration landscapes, and ion dynamics throughout the LATP composition space while accelerating potential-energy-grid calculations and MD simulations by more than two orders of magnitude relative to density functional theory (DFT).

This limited need for fine-tuning and computational efficiency provided by the resulting MLIP enables systematic exploration of large disordered supercells, extensive configurational sampling, and simulation times sufficient to reach the diffusive regime and obtain converged diffusion coefficients. The individual components of the workflow are described in the following sections.

2.1 Structure generation

As a starting point, the conventional rhombohedral unit cell of $\text{LiTi}_2(\text{PO}_4)_3$ (total formula $\text{Li}_6\text{Ti}_{12}\text{P}_{18}\text{O}_{72}$, lattice parameters $a = b = 8.622 \text{ \AA}$, $c = 21.0816 \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$) was obtained from the Materials Project database.[19, 20] Substituted configurations were generated by constructing a $2 \times 2 \times 1$ supercell of the conventional unit cell and randomly replacing subsets of Ti atoms with Al. To avoid redundant configurations, each generated structure was checked for symmetry equivalence with respect to previously accepted configurations using the space group operations of the parent structure. Configurations found to be symmetry-equivalent to existing ones were discarded and replaced by newly generated random configurations. Using this procedure, five distinct configurations were generated at each substitution level $x \approx 0.17, 0.33, 0.50, 0.67, 0.83, 1.00, 1.17, 1.33, 1.50, 1.67$, and 1.83 in $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$. These correspond to 4, 8, 12, 16, 20, 24, 28, 32, 36, 40, and 44 Ti-to-Al substitutions, respectively, out of the 48 available Ti sites in the $2 \times 2 \times 1$ supercell.

2.2 Foundation-model fine-tuning and transferability

To obtain the final MACE models, the MACE-MPA0 foundational model was fine-tuned using single-particle grid and ab initio molecular dynamics (AIMD) data generated from density functional theory (DFT) calculations of the symmetric LATP structure at $x = 0.33$. A central objective was to assess whether a foundation model fine-tuned using data from a single composition can accurately describe the full LATP substitution space. This provides a stringent test of transferability across varying carrier concentrations, framework compositions, and local disorder environments.

Two MACE models were trained on energies and forces: one for single-particle grid calculations and one for molecular dynamics (MD) simulations. The training data was created by performing DFT calculations with the CP2K software package [21] (version 2023.1), using the PBE functional [22], Goedecker–Teter–Hutter pseudopotentials [23–25], and DZVP-MOLOPT-SR-GTH basis sets [26]. For the grid model, the training set was constructed from approximately 800 configurations derived from the LATP single-particle energy grid computed according to our previous work.[17] Starting from the full grid, symmetry-equivalent configurations were reduced to a single representative structure and configurations with energies more than 3 eV above the global minimum were discarded, as such high-energy states are rarely sampled under relevant conditions. Training on configurations within this energy range was sufficient to achieve good extrapolation up to approximately 10 eV. For the MD model, the training set consisted of 500 configurations sampled from the reduced grid dataset combined with approximately 500 equally spaced frames from an AIMD trajectory.

The inclusion of grid-based configurations ensures adequate representation of migration barriers, which are typically under-sampled in equilibrium AIMD simulations. Fine-tuning was performed for up to 10 epochs using equal weighting of energies and forces, a learning rate of 0.001, and a validation split of 15%.

The transferability of the resulting grid model was evaluated for supercells, geometry-optimized structures, and a range of substitution concentrations. The model demonstrates good extrapolation across these conditions, as confirmed by comparison to DFT reference energies, which is discussed in Section 3.1 with additional data provided in the "MACE model validation" section of the Supporting Information.

2.3 Ionic TuTraSt calculations

The Ionic TuTraSt approach is a previously developed workflow for efficient calculation of diffusion properties of mobile ions in periodic frameworks.[16] It consists of constructing an effective three-dimensional potential energy landscape for the mobile ion species, followed by topological analysis using the TuTraSt algorithm to extract connectivity information. This information is used to automatically construct lattice kinetic Monte Carlo (kMC) models, from which diffusion coefficients are obtained.[27]

Within this framework, the effective potential energy, referred to as the multi-particle potential energy, is constructed by separating the contributions into Li^+ -framework and Li^+ - Li^+ interactions. The former is obtained from a single-particle potential energy landscape, while the latter is incorporated through statistical sampling of interacting ions. The single-particle potential is first evaluated on a three-dimensional grid, after which the full multi-particle potential energy surface is obtained by sampling configurations of interacting Li^+ ions using Metropolis Monte Carlo simulations.

Detailed computational parameters for each step are given below. For a comprehensive description of the TuTraSt algorithm and the Ionic TuTraSt method, we refer to the original works.[16, 27]

2.3.1 Single-particle energy grid calculations

The single-particle energy grids used as input to the Ionic TuTraSt workflow were calculated following a procedure consistent with our previous work.[17] The single-particle potential energy is defined as the energy of a single Li^+ ion as a function of its position within the $\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ framework, with all other Li^+ ions removed.

The energy was evaluated on a three-dimensional grid with a spacing of approximately 0.4 Å in fractional coordinates, using the grid-trained MACE model described in Section 2.2. For each grid point, a Li^+ ion was inserted into the framework and the total energy was computed. Grid points within a spherical cutoff of 0.7 times the van der Waals radius of any framework atom were excluded to avoid unphysical configurations. For highly symmetric end members (LTP and LAP), space group symmetry was used to reduce the number of unique grid points calculations.

2.3.2 Multi-particle grid calculations

Multi-particle free energy grids were constructed from Li^+ probability distributions obtained from Metropolis Monte Carlo (MMC) simulations within the Ionic TuTraSt framework. Simulations were carried out in the NVT ensemble at 1000 K using the stoichiometric number of interacting Li^+ ions in an otherwise empty simulation cell.

Li^+ – Li^+ interactions were modeled using a Lennard-Jones potential with parameters from the Universal Force Field,[28] combined with a partial charge of $q_{\text{Li}} = +0.5e$, treated using Ewald summation. The Li^+ –framework interactions were obtained directly from the precomputed single-particle grids.

Following equilibration for 10^5 steps, production runs between 1.4×10^6 and 3.3×10^7 cycles were performed. The multi-particle potential energy grids $E_{MP}(r_i)$ were then obtained from the resulting Li^+ probability density $P(r_i)$ using the Boltzmann relation,[16]

$$E_{MP}(r_i) = -k_B T \ln P(r_i) \quad (1)$$

2.3.3 TuTraSt analysis

The resulting multi-particle energy grids were analyzed using the TuTraSt algorithm.[27] Breakthrough energies were determined using an energy increment of 2 kJ/mol (0.02 eV) and an energy cutoff of 400 kJ/mol (4.15 eV). For the construction of coarse-grained lattice kMC models, a larger increment of 5 kJ/mol (0.05 eV) and a cutoff of 100 kJ/mol (0.104 eV) were used. This choice ensures stable coarse-graining by excluding transitions with negligible barriers in certain regions of the PES.

From these models, 30 independent kMC trajectories of 10^6 steps each were simulated at 1000 K. Diffusion coefficients were computed from the slope of the mean squared displacement (MSD) using the Einstein relation,

$$\text{MSD}(t) = \langle (\mathbf{r}(t) - \mathbf{r}_0)^2 \rangle = 6D_0 t \quad (t \rightarrow \infty) \quad (2)$$

where the fitting window was chosen between the times at which the MSD exceeded one and two unit cell lengths along the corresponding direction. Final diffusion coefficients and their uncertainties were obtained as the mean and standard deviation over all trajectories.

2.4 Molecular dynamics simulations and geometry optimization

The MD-trained MACE model was used to perform MD simulations on randomly selected configurations at Al concentrations $x = 0.17, 0.33, 0.50, 0.67, 1.33$, and 2.0. To assess the impact of framework dynamics, simulations were carried out both with a fixed framework and with fully flexible framework atoms.

All MD simulations were performed using the LAMMPS package [29] in the NVT ensemble with a Nosé–Hoover thermostat and a timestep of 2 fs. Each system was equilibrated for 20 ps, followed by a production run of 0.5 ns. This simulation length enables statistically reliable determination of diffusion coefficients, which were extracted from the mean squared displacement using the Einstein relation (Equation 2). In addition,

the Li^+ probability density was computed and converted into a free-energy landscape using the Boltzmann relation (Equation 1). Partial Li–O radial distribution functions (RDFs) were also calculated to quantify changes in Li–O interactions.

Geometry optimizations were performed on structures equilibrated using fixed-framework MD in order to obtain representative Li^+ configurations. Two optimization protocols were considered: (i) isotropic cell relaxation combined with full relaxation of all atomic positions (GeoOpt), and (ii) isotropic cell relaxation with fixed framework atomic positions (CellOpt). To quantify the impact of these structural changes, simulation cell volumes were extracted for all systems. In addition, effective REPEAT charges[30] were computed for both initial and geometry-optimized structures using single-point DFT calculations with the same settings as used for the training data. These charges provide an interpretable measure of how the electronic structure evolves with substitution and structural relaxation.

3 Results and Discussion

The results address two mechanistic questions: which effects of Al substitution enhance Li^+ diffusion at low substitution levels, and which are required to explain its decline at higher Al content? We first assess the transferability of the fine-tuned potential beyond its training composition. We then separate the effects of framework chemistry and Li^+ loading at fixed structure, before introducing framework dynamics and composition-dependent structural relaxation. This sequence establishes which features of the transport trend each contribution can explain and where additional physical effects become necessary.

3.1 Transferability of the Fine-Tuned Potential

To explore the transferability of the fine-tuned MACE model, trained on a single LATP grid at the concentration $x = 0.33$, the predictions of the model are compared to the energies obtained from DFT for different substitution concentrations, supercells as well as cell- and geometry-optimized structures.

The parity plots in Fig. 2 illustrate the transferability of the fine-tuned grid model. The model was trained on grid points with energies ≤ 3 eV above the minimum energy and shows good extrapolation up to 10 eV. The performance on the combined training and test set is illustrated in Fig. 2a, indicating that the fine-tuning has converged. When the model is applied to supercells (Fig. 2b), there is almost no loss of accuracy, which underlines that the size of the simulation cell, which was used for training, is large enough.

The model transfers well across changes in composition, substitutional arrangement, and structure, with the largest deviations occurring at the Al-rich end of the compositional range. Accuracy is retained for pure LTP (Fig. 2c), whereas LAP, the composition furthest from the training system, shows slight underestimations of energies. Nevertheless, the relative ordering of energies is preserved (Fig. 2d). Different Ti/Al arrangements introduce only a modest increase in error (Fig. 2e), while cell and atomic relaxation leave the accuracy largely unchanged (Fig. 2f).

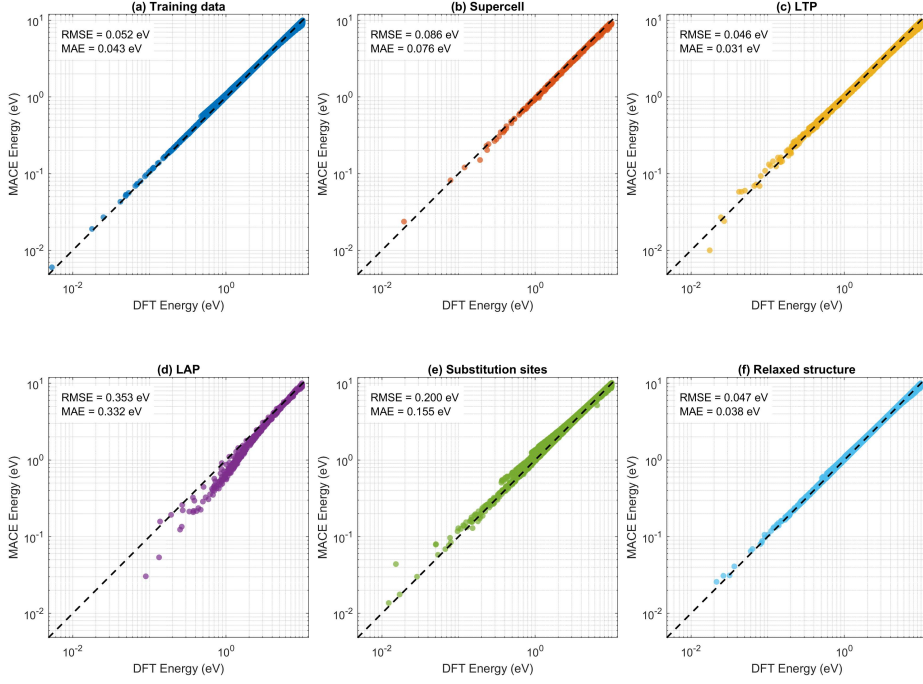


Fig. 2 Representative parity plots illustrating the transferability of the fine-tuned grid model. Errors are calculated from all energies ≤ 3 eV. Comparing the energies from the finetuned model with DFT reference energies for (a) the $x = 0.33$ system (includes 800 training data points) (b) $2 \times 2 \times 2$ supercell (c) LTP ($x = 0$) (d) LAP ($x = 1$) (e) randomly placed substitution sites (f) geometry-optimized structure.

Together, these comparisons support the transferability of the fine-tuned potential to larger supercells, disordered substitutional configurations, and relaxed structures. The main limitation is a tendency to underestimate migration barriers at high Al content. However, transport in this regime also reflects the increased Li^+ concentration and associated ion-ion interactions, which influence diffusion more strongly than changes in the framework potential alone (see Section 3.3 and “Independent variation of Li and Al concentrations” in the Supporting Information). The significance of the single-particle energy errors should therefore be assessed in the context of the interacting-ion system, although they remain a source of uncertainty in the transport predictions.

3.2 Effect of Ion–Framework Interactions

The single-particle potential energy surfaces isolate the interaction between Li^+ ions and the framework. These grids reveal how the framework potential alone shapes the energy landscape, without contributions from $\text{Li}^+ - \text{Li}^+$ interactions or structural relaxation effects.

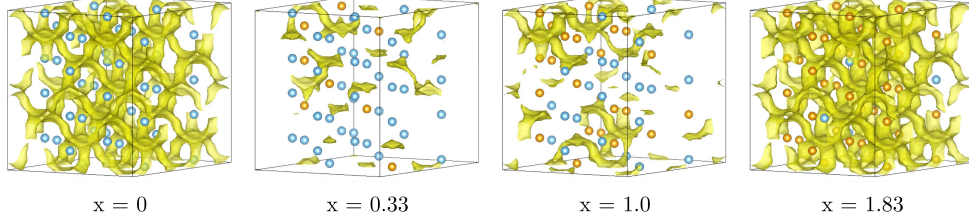


Fig. 3 Isosurfaces at $E = 1.5$ eV of the single-particle PES for $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ at the indicated values of x . Ti atoms (blue) and Al atoms (orange) are shown, while P and O atoms are omitted for clarity.

Isosurfaces at $E = 1.5$ eV of the single-particle PES for LTP and representative LATP configurations with increasing Al content are shown in Fig. 3. For LTP, the PES exhibits a symmetric and regular network of percolating channels at this energy level, connecting the M1 sites corresponding to energy minima located at sixfold coordinated junctions. For LATP compositions ($x = 0.33$ and $x = 1.0$), the low-energy basins are primarily located in the vicinity of Al substitutions, while basins further away from Al sites appear only at higher energies. This indicates that Li^+ positions adjacent to Al are energetically stabilized relative to those surrounded by Ti. This observation is consistent with previous findings that Al substitution induces a trapping effect, which can be attributed to the lower charge of Al^{3+} compared to Ti^{4+} , leading to stronger electrostatic attraction between AlO_6 octahedra and Li^+ ions.

At intermediate Al concentrations, localized connections begin to form between Al-stabilized sites. For $x = 1.0$, such pathways start to percolate in certain directions, while for $x = 1.83$ they extend throughout the entire structure, forming a fully connected network. These percolating pathways are consistently located adjacent to one or more Al atoms, indicating that Al substitution also stabilizes transition-state regions between Li sites. This local barrier-lowering effect has previously been demonstrated using DFT-NEB calculations for interstitial migration mechanisms.[7] However, for randomly distributed substitutions, this effect does not percolate uniformly across all directions at intermediate concentrations. Consequently, the net effect of Al substitution on the framework potential is concentration dependent: at low concentrations, trapping dominates and impedes diffusion, while at sufficiently high concentrations, the overlap of “Al-stabilize” regions leads to the formation of continuous low-energy pathways that facilitate diffusion.

To quantify these effects, we analyze the breakthrough energy E_{BT} of the single-particle PES, defined as the energy at which a percolating pathway forms across the unit cell in a given direction, relative to the global minimum.

The breakthrough energies shown in Fig. 4 provide a quantitative measure of the global impact of Al substitution on the energy landscape. At low substitution levels, E_{BT} increases sharply (by ~ 1 eV) relative to LTP, directly reflecting the trapping effect. Across the range $0.17 \leq x \leq 0.67$, the breakthrough energy remains elevated and exhibits a large spread, indicating strong sensitivity to the specific arrangement of Al atoms.

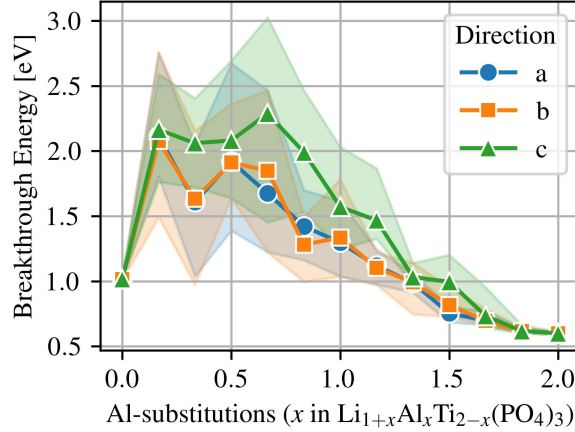


Fig. 4 Breakthrough energies of the single-particle PES as a function of composition, defined as the lowest energy at which percolating pathways connect opposite faces of the unit cell. Markers show averages over five configurations, and shaded regions indicate the range between minimum and maximum values.

This sensitivity arises from the configurational variability of local Al environments. At low concentrations, clustered Al substitutions can create strongly stabilized regions that localize Li^+ ions, while simultaneously generating Ti-rich regions where percolation is suppressed, resulting in higher E_{BT} . In contrast, a more uniform distribution of Al leads to a more homogeneous energy landscape and lower breakthrough energies, although the probability of forming percolating low-energy pathways remains low in this regime. As a result, even favorable local arrangements do not typically lead to global connectivity at low Al concentrations.

At higher substitution levels ($x > 0.67$), E_{BT} decreases and its variability diminishes. This reflects the increasing likelihood that Al-stabilized regions overlap and form connected diffusion pathways. In terms of the diffusion network, this behavior can be understood within the framework of percolation theory[31] as the percolation of M2 interstitial sites, which requires neighboring Al substitutions. In the underlying simple cubic arrangement of M1 sites, each M1 site is coordinated by two Al/Ti sites (one above and one below), and an M2 connection forms when the top site of one M1 site and the bottom site of a neighboring M1 site are both occupied by Al, or vice versa. This connectivity can be described by a two-layer simple cubic lattice model, which yields a percolation threshold of $p_c \sim 0.43$, corresponding to $x \sim 0.86$, in reasonable agreement with the observed trend.

Overall, these results show that Al substitution primarily introduces a trapping effect at low concentrations, which raises the breakthrough energy and hinders diffusion. As the Al concentration increases, these trapping regions begin to overlap, eventually forming percolating low-energy channels that flatten the single-particle PES and facilitate diffusion.

These findings also highlight the limitations of methods that probe only restricted portions of the potential energy surface. Approaches based on minimum energy pathways, such as NEB, or simulations constrained to small periodic unit cells, such as

conventional AIMD, are unable to fully capture substitutional disorder and the resulting configurational variability. While single-particle grid methods provide access to complete migration networks, they are constructed from static configurations and therefore do not account for ion–ion interactions or dynamical effects. Consequently, ion–ion correlations, framework flexibility, and configurational entropy are not fully represented, underscoring the limitations of such approaches in describing global Li^+ diffusion mechanisms.

3.3 Effect of Li^+ Loading on the Free Energy Landscape

The effects of Li^+ concentration and ion–ion interactions are analyzed by comparing multi-particle potential energy surfaces from the Ionic TuTraSt workflow with the corresponding single-particle PES. This comparison separates the contributions from the ion–framework and ion–ion interactions, respectively. Independent calculations of diffusion coefficients as a function of Al content and Li^+ concentration further clarify how these factors govern ion migration across the compositional range. Structural changes and framework flexibility are excluded here and addressed in later sections, allowing trends related to ion concentration and chemical environment to be assessed independently within the LATP framework.

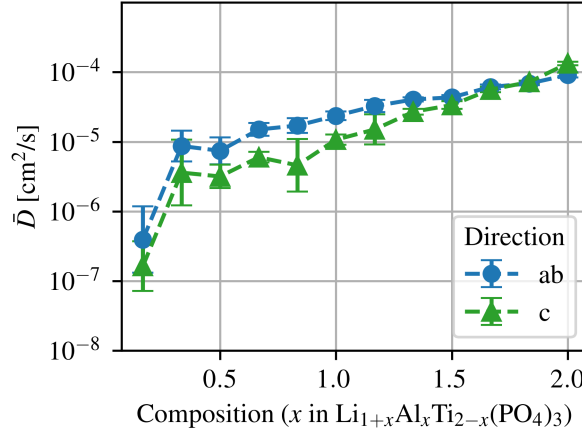


Fig. 5 Diffusion coefficients predicted from Ionic TuTraSt at stoichiometric conditions (Li content matching Al content) for substituted $2 \times 2 \times 1$ supercells of LTP. Values are averaged over five configurations at each composition (except $x = 2.0$, LAP, with a single configuration).

Fig. 5 shows the Li^+ self-diffusion coefficients predicted by Ionic TuTraSt as a function of stoichiometric composition, averaged over five configurations at each composition. The diffusion increases almost monotonically with increasing x , with the largest relative increase occurring from low x up to $x = 0.33$. Since only the number of Li^+ ions and Al atoms varies while the structure remains fixed, this trend must arise from changes in the Li–framework interactions and/or from Li^+ – Li^+ interactions. Notably, these effects alone do not produce a decrease in diffusion at higher x . In light

of the single-particle PES analysis, where Al induces a trapping effect at low and intermediate substitution levels, the increase in diffusion observed in Fig. 5 is unexpected if the framework contribution were dominant. This instead indicates that additional Li^+ ions and the resulting ion-ion interactions play a dominant role in this regime. Further support is provided by the breakthrough energies of the multi-particle PES (Fig. 6), which represent the effective energy landscape in the presence of multiple ions. These energies capture the combined influence of the framework potential and ion-ion interactions, while deviations from the single-particle breakthrough energies provide a measure of the effect of multi-ion occupancy.

Relative to the single-particle case, LTP is the only composition where the breakthrough energy increases. Here, all Li^+ ions occupy low-energy sites, and ion-ion repulsion stabilizes this ordered configuration, making interstitial occupation or vacancy formation energetically unfavorable. For all other compositions, the breakthrough energy decreases significantly, demonstrating the effect of additional Li^+ ions. This is consistent with the comparison of single- and multi-particle PES isosurfaces (Fig. 3 and Fig. 7), where Al-stabilized regions remain but become more delocalized. Notably, the largest decrease in breakthrough energy occurs over the first three compositions (up to $x = 0.33$), after which the decline becomes more gradual. This behavior contrasts with the single-particle PES, where breakthrough energies begin to decrease only at $x \geq 0.67$ and exhibit significant variability at low Al content. Neither the pronounced initial decrease nor the large variability observed in the single-particle case is present in the multi-particle PES, further highlighting the dominant role of ion-ion interactions in governing diffusion in this regime. The nearly constant breakthrough energy at $x \geq 0.33$ can instead be understood in terms of percolation of M1/2 split sites. Each additional Li^+ ion effectively splits an M1 site into M1/2 sites. Since the M1 sites form a simple cubic lattice, this system can be described by a site-percolation model with a threshold of $p_c \sim 0.31$.^[31] This corresponds to a Li^+ concentration of $x \approx 0.31$, indicating the onset of percolation of split-site pathways.

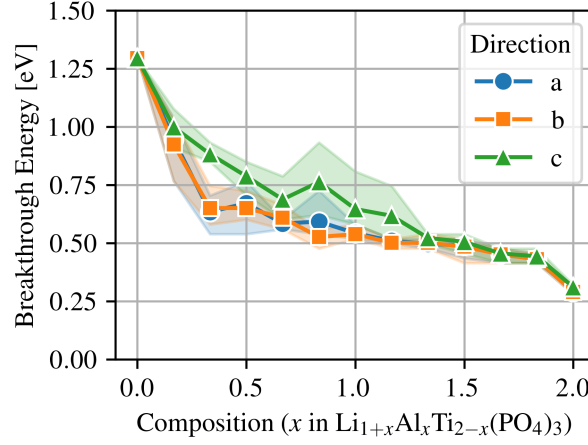


Fig. 6 Breakthrough energies of the multi-particle PES as a function of composition, defined as the lowest energy at which grid points up to this level form percolating connected components joining opposite faces of the unit cell. Markers show averages over configurations (five for intermediate compositions; one for $x = 0.0$ and $x = 2.0$), and shaded regions indicate the range between minimum and maximum values.

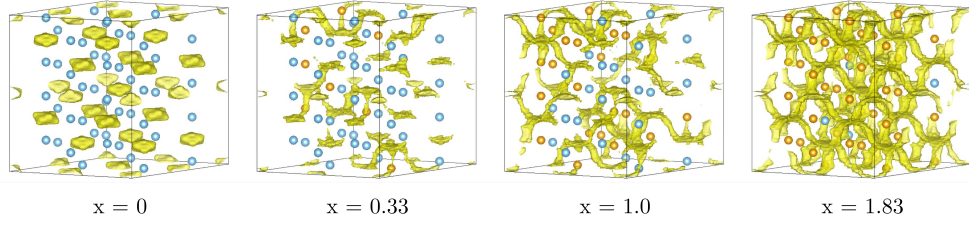


Fig. 7 Isosurfaces of the multi-particle PES at 0.6 eV for four stoichiometric compositions of $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$. Ti atoms (blue) and Al atoms (orange) are shown, while P and O atoms are omitted for clarity.

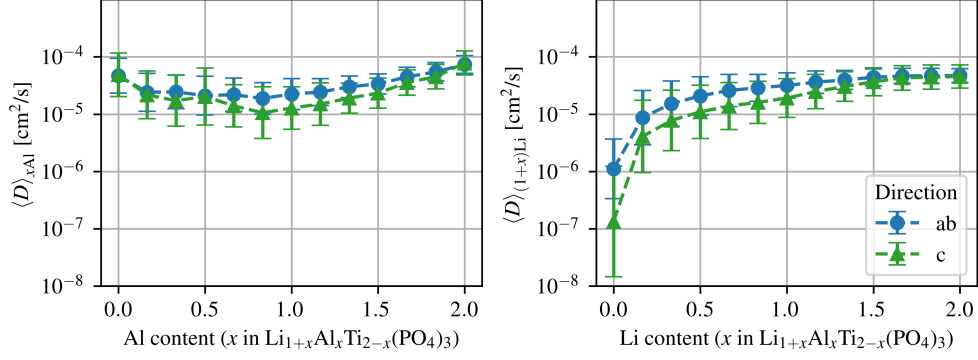


Fig. 8 Diffusion coefficients in the ab and c directions. Left: averages over all Li^+ concentrations plotted versus Al content ($\langle D \rangle_{xAl}$). Right: averages over all Al concentrations plotted versus Li^+ content ($\langle D \rangle_{(1+x)Li}$).

To more directly compare the effects of Al substitution and Li^+ content, multi-particle grids were generated for all combinations of both variables. Although artificial, this approach enables the two effects to be examined more independently. The data are reduced by averaging over one parameter while retaining dependence on the other, yielding $\langle D \rangle_{xAl}$ and $\langle D \rangle_{(1+x)Li}$. Fig. 8 shows $\langle D \rangle_{xAl}$ as a function of Al content and $\langle D \rangle_{(1+x)Li}$ as a function of Li^+ content. Averaging over Li^+ concentrations reveals only a weak dependence of diffusion on Al, with a shallow minimum near the midpoint of the compositional range and local maxima at the end members. This behavior is consistent with the single-particle PES and indicates a residual trapping effect associated with Al, even when Li^+-Li^+ interactions are included. In contrast, averaging over Al content shows a clear increase in diffusion with increasing Li^+ concentration, demonstrating that Li^+ loading has a stronger influence on diffusion than changes in the framework composition. Fig. S1 and S2 show that these trends persist for individual compositions.

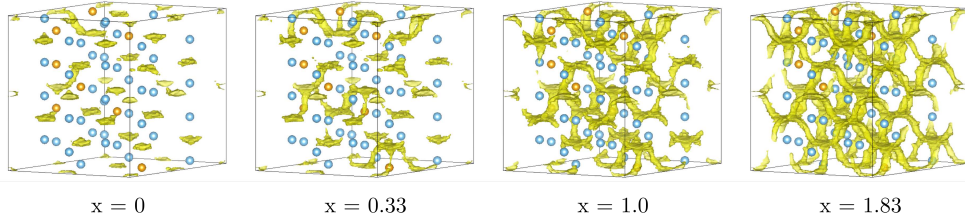


Fig. 9 Isosurfaces of the multi-particle PES at 0.6 eV for a structure with eight Al substitutions, shown for different Li^+ contents corresponding to $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ with $x = 0, 0.33, 1.0,$ and 1.83 . Ti atoms (blue) and Al atoms (orange) are shown.

The relative effect of increasing Li^+ content is largest between $x = 0$ and $x = 0.17$, i.e. at low substitution levels, and becomes small beyond $x \approx 1.5$. Fig. 9 illustrates

how variations in Li^+ content modify the PES at fixed composition ($x = 0.33$). The introduction of additional Li^+ ions leads to the emergence of new migration pathways and modifies migration barriers through Li^+ -Li interactions, explaining why the initially added Li^+ produces the largest relative increase in diffusion. In the unsubstituted structure, Li^+ ions are accommodated within available low-energy sites. Adding additional Li^+ disrupts this arrangement, leading to splitting of M1 sites into M1/2 configurations and enhanced ion-ion interactions, consistent with interstitial migration mechanisms reported previously.[7] As the Li^+ content increases further, these effects extend over a larger fraction of the structure, involving more ions and available sites, before eventually saturating at high substitution levels.

3.4 Effect of Framework Flexibility

Fig. 10 shows diffusion coefficients obtained from MD simulations, where one representative configuration (system A) was selected for each substitution level. Results for all five configurations at $x = 0.33$ are provided in the Supporting Information and show very similar diffusion coefficients, with variations within $\pm 10\%$ of the mean (see Fig S9 in the Supporting Information). The left panel of Fig. 10 compares diffusion coefficients from simulations with fixed and flexible frameworks. With a fixed framework, the diffusion coefficient increases continuously with substitution concentration, whereas for a flexible framework it plateaus around $x \approx 0.5$. A pronounced difference between the two cases is observed at low substitution levels, which gradually diminishes with increasing x . This indicates that framework dynamics play an important role at low concentrations, while ion-loading effects become dominant at higher substitution levels.

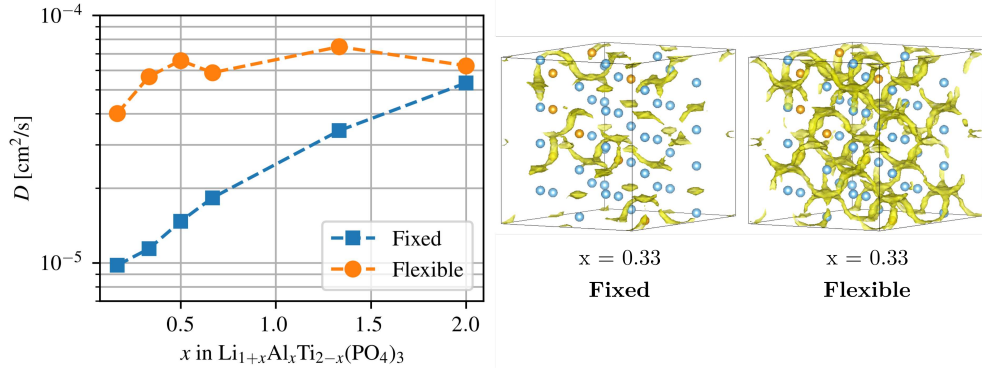


Fig. 10 Diffusion coefficients and free-energy isosurfaces illustrating the effect of framework flexibility. Left: Li^+ diffusion coefficients as a function of composition, obtained from MD simulations with fixed and flexible frameworks. Right: free-energy isosurfaces at $E = 0.3$ eV for the composition $x = 0.33$, obtained from MD-sampled probability densities. Ti atoms (blue) and Al atoms (orange) are shown.

The right panel of Fig. 10 compares the free-energy isosurfaces at $E = 0.3$ eV for the system at $x = 0.33$, obtained from the fixed and flexible framework MD simulations, respectively. When the framework is flexible, the energy barriers are reduced and the diffusion channels are wider compared to the fixed-framework case, consistent with previous work on the role of lattice dynamics in ceramic electrolytes.[14] Lower energy barriers are particularly evident near Al substitution sites, consistent with the Al-induced stabilization observed in the single- and multi-particle PES analyses. This effect is pronounced when the framework is held fixed, indicating that local ion-framework interactions affect the effective energy landscape of the Li^+ ions. However, these local variations are less reflected in the diffusion coefficients when framework flexibility is included. This suggests that at higher substitution levels, where chains of AlO_6 octahedra begin to percolate, the influence of Li^+ - Li^+ interactions dominates over local framework effects in determining long-range transport.

These results show that framework flexibility significantly influences the effective diffusion pathways in LATP at low substitution levels, while its impact diminishes as increasing Al content enhances the role of Li^+ - Li^+ interactions. However, these effects alone do not account for the experimentally observed decrease in conductivity at $x > 0.33$, indicating that additional mechanisms beyond those captured in the present simulations contribute to limiting ion transport in this compositional range.

3.5 Effect of Cell Relaxation

Al substitution modifies the structure both globally, through changes in cell parameters and volume, and locally, through alterations of atomic geometries. These changes arise from differences in ionic radius and charge between Al and Ti, as well as from the additional Li^+ ion introduced during substitution. To evaluate the impact of these structural changes on Li^+ diffusion, we compare six compositions at their initial LTP geometries and at optimized geometries obtained from two schemes: CellOpt, where the cell parameters a , b , c , and γ are relaxed; and GeoOpt, where both the cell and atomic positions are relaxed.

Although the Ionic TuTraSt approach is restricted to a fixed-framework approximation and therefore does not capture dynamic framework flexibility, it can still be used to assess the effect of static structural changes such as variations in cell volume and atomic arrangement. Fig. 11 shows the predicted Li^+ diffusion coefficients for the three sets of structures as a function of composition. The results obtained after cell-only relaxation (CellOpt) are, in most cases, very similar to those of the initial structures, indicating a negligible effect on Li^+ transport within this model. In contrast, for the fully relaxed structures (GeoOpt), the overall compositional trends are preserved, but the magnitude of the diffusion coefficients decreases by approximately 0.5–1.0 orders of magnitude, corresponding to a systematic reduction in diffusion across all compositions.

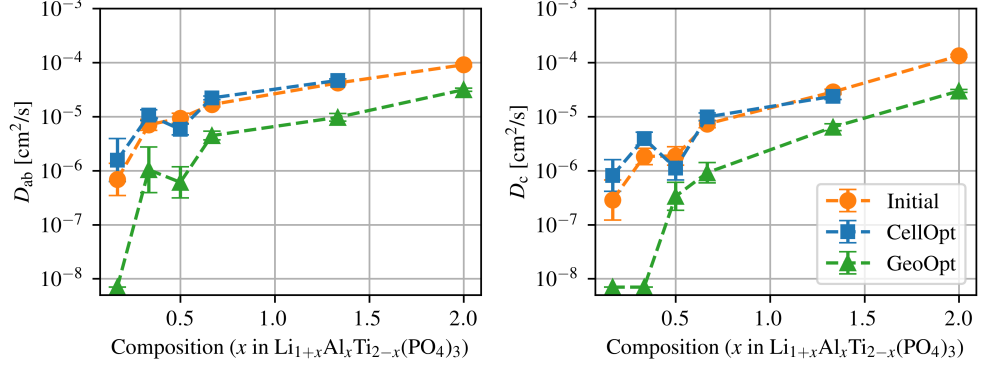


Fig. 11 Diffusion coefficients predicted from Ionic TuTraSt at stoichiometric conditions (Li^+ content in MMC matching Al content) as a function of composition, for initial and optimized LATP structures. Left: averaged self-diffusion in the a and b directions (D_{ab}). Right: self-diffusion in the c direction (D_c). Values below $10^{-8} \text{ cm}^2/\text{s}$ indicate either the absence of percolating diffusion channels below the energy cutoff or that the MSD did not reach the diffusive regime.

The decrease in diffusion predicted by Ionic TuTraSt for the GeoOpt structures suggests that local atomic rearrangements can have a detrimental effect on the fixed framework description of the ionic dynamics. During geometry optimization, the framework relaxes to minimize the energy for a specific, static Li^+ configuration. This stabilizes occupied sites and deepens their energy basins, while not accounting for the broader ensemble of accessible configurations. As a result, migration barriers increase, and symmetrically equivalent but unoccupied sites may appear less favorable. This indicates that experimentally determined structures, which represent averaged atomic arrangements, are better suited for such analyses, whereas full atomic relaxation can introduce artifacts into the PES and bias diffusion predictions. Similar effects should also be considered in NEB calculations, where local relaxations are typically included. These effects are likewise reflected in the fixed-framework MD simulations discussed below.

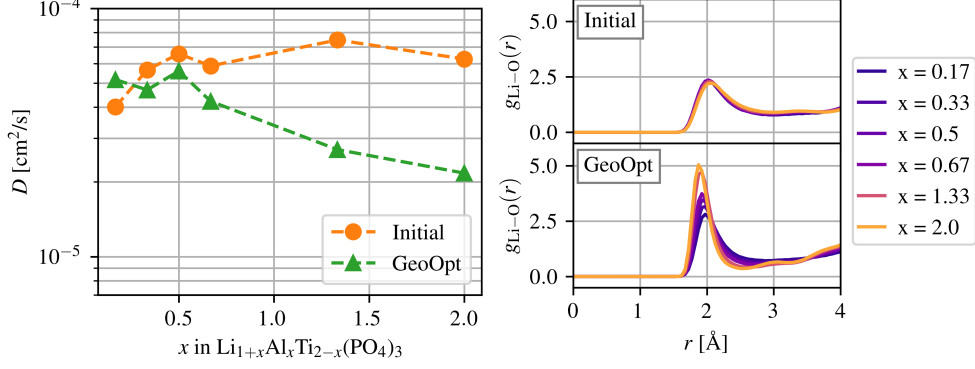


Fig. 12 Impact of local and cell rearrangements. Left: diffusion coefficients from MD simulations for initial and geometry-optimized (GeoOpt) structures. Right: Li–O radial distribution functions for different substitution levels for initial (top) and optimized (bottom) structures.

The left panel of Fig. 12 compares diffusion coefficients from flexible-framework MD simulations using GeoOpt structures as initial configurations with those obtained from the non-optimized structures. As the framework atoms are dynamically propagated during the MD simulations, relaxing atomic positions prior to the simulation does not directly affect the outcome; only changes in the cell parameters, which remain fixed during MD, influence the results. For the optimized structures, a clear decrease in the diffusion coefficient is observed for $x > 0.5$. This indicates that relaxation of cell parameters for each Al concentration, in combination with explicitly accounting for the dynamics of the framework, is necessary to reproduce the experimentally observed decrease in Li^+ conductivity at high Al contents. To further elucidate the origin of this trend, we analyze the radial distribution functions (RDFs) obtained from both the geometry-optimized and non-optimized simulations across the full range of x values.

The top right panel of Fig. 12 shows that the Li–O radial distribution function (RDF) is nearly identical across all substitution concentrations for the non-optimized structures. In contrast, the optimized structures (bottom right panel of Fig. 12) exhibit a systematically higher first RDF peak, with the peak height increasing with substitution concentration. The reduced diffusion at higher substitution levels can be rationalized by two related observations. First, as shown in the Supporting Information Fig. S11, the cell volume of the optimized structures decreases with increasing substitution concentration. Second, the RDFs indicate stronger Li–O interactions. To support this interpretation, effective REPEAT charges[30] were calculated for both the initial and optimized structures (see Fig. S10 in the Supporting Information). These show that oxygen carries a significantly more negative charge in the optimized structures, while the change in the Li charge is comparatively small. This provides a microscopic explanation for the stronger Li–O interactions. A similar trend has been reported in the related compound LAGP, where Ti is replaced by Ge, and changes in Li–O interactions with increasing Al substitution were observed.[32]

Additional results (see Fig. S12) show that CellOpt structures (cell relaxation only) yield diffusion coefficients similar to GeoOpt structures when framework dynamics are

included. In contrast, when the framework is fixed, CellOpt leads to a general reduction in diffusion but does not reproduce the decrease observed at high substitution levels. This confirms that cell relaxation alone is insufficient and that local rearrangements and framework dynamics must be considered.

Even small structural differences can have a pronounced impact on diffusion. For example, at $x = 1.33$, the initial and GeoOpt structures exhibit nearly identical cell parameters but significantly different diffusion coefficients. This highlights the sensitivity of diffusion to subtle structural distortions, which may also contribute to the variability observed in TuTraSt calculations and experiments. When the framework is fixed, diffusion is highly sensitive to such small changes, whereas for flexible frameworks this sensitivity emerges only at higher substitution levels ($x > 0.5$).

The results suggest that while reduced cell volume contributes to lower diffusion, the stronger Li–O interactions arising from local structural asymmetries and enhanced electrostatic interactions play a key role in limiting ion mobility at high substitution levels. Crucially, these effects are only observed when the framework atoms are mobile. While such structural changes may partly explain the experimentally observed decrease in conductivity, additional factors in real materials such as Al aggregation, phase separation, structural transitions, and defects, are also expected to contribute.

4 Conclusion

In this work, we combined a fine-tuned machine-learning foundation potential, energy-landscape analysis, and molecular dynamics simulations to investigate Li-ion transport across the complete compositional range of $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$. This enabled the systematic separation of carrier-concentration, framework-chemistry, and structural contributions to diffusion while explicitly accounting for substitutional disorder and long-timescale ion dynamics.

Our results show that increased Li^+ concentration is the primary factor enhancing diffusion throughout the substitution range. Although Al substitution modifies the framework potential by locally stabilizing Li^+ ions and creating heterogeneous energy landscapes, these effects alone do not explain the observed transport trends. Instead, ion-ion interactions associated with increasing carrier concentration dominate the enhancement of diffusivity, particularly at low to intermediate substitution levels. The reduction in diffusivity at high Al contents emerges only when substitution-induced structural changes are considered and is associated with reduced cell volume, stronger Li-O interactions, and local framework rearrangements. Together, these competing effects provide a mechanistic explanation for the non-monotonic transport behavior observed experimentally in LATP.

Beyond the specific case of LATP, this work demonstrates how foundation machine-learning potentials can be used to explore compositionally and configurationally complex materials spaces with near first-principles accuracy. By fine-tuning a foundation model using data from a single composition, we obtained a transferable interatomic potential capable of accurately describing structures, energetics, migration landscapes, and ion dynamics across the entire substitution range. This capability enabled the investigation of large disordered systems and diffusion processes that would be prohibitively expensive using conventional first-principles methods.

More broadly, the workflow presented here provides a general strategy for disentangling the coupled effects of carrier concentration, chemistry, structure, and disorder in aliovalently substituted ionic conductors. We anticipate that this approach will be applicable to a wide range of compositionally complex solid electrolytes and other disordered functional materials, where understanding structure-transport relationships requires atomistic sampling across broad configurational spaces.

Supplementary information. The following files are available free of charge.

- SI.pdf: Additional computational details and analysis results.

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Data Availability Statement. The datasets generated and/or analysed during the current study are included in this published article and its supplementary information

files or are available in the "SupplementaryData.LATP" github repository, <https://github.com/EnGeo-Team/SupplementaryData.LATP>.

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